SUPPORTING INFORMATION

"Natural Attenuation of Arsenic by Sediment Sorption and Oxidation"

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I. Experimental Section

Sediment Collection and Analyses

The sediment core used in this study (SMW-3) was collected during coring at the Ft. Devens site on April 20-24, 2006. Borings were drilled from the ground surface to a depth of ~44.2 m; sections of core material 0.3 m in length were isolated by slicing the core and pushing a 5 cm outside diameter (OD) acetate tube 0.3 m into the end of the core, slicing the other end of the section to isolate the sample, capping both ends of the acetate tube, and securing the caps with duct tape. This procedure was intended to limit the exposure of aquifer material to atmospheric oxygen. Sample cores were stored in a dark and cool (4°C) place, shipped to the laboratory within 24 h in a cooler packed with ice, and frozen immediately upon arrival. Sediment core samples were defrosted, sectioned, and homogenized inside a nitrogen (N_2) glove box. Sub-samples were then refrozen for later use in extraction and mobilization experiments.

Sediment sub-samples were extracted following the EPA 3050B extraction method *(1)*, which is not a total digestion but is designed to estimate "environmentally available" metal contents of sediments (see He et al. *(2)*, for details). The extractions were conducted on 1-2 g (wet weight) sediment in triplicate and can be briefly described as follows: digestion at 95±5 °C with 10 mL of 1:1 HNO_3 for 10-15 min and with 5 mL of concentrated HNO_3 for 2 h; digestion with 30% H_2O_2 (added in approximately 1-mL increments until the reaction was complete) and heating to reduce the volume to approximately 5 mL; dilution to 50 mL volume with H_2O and centrifugation at 3,000 rpm for at least 10 min to separate any remaining particulate matter; dilution of supernatant with 2% (v/v) HNO_3 for ICP-MS analysis. Throughout the digestion procedure, the vessel was loosely covered and the bottom of the vessel was always covered with solution. Water content was determined gravimetrically for each sediment sample.

Total arsenic concentrations in sediments were also measured by total digestion using hydrofluoric acid. All reagents were trace metal grade. The samples were digested in an Anton Parr Microwave 3000 operating at 1400 W at 100% output, and equipped with a pressure controller, IR temperature monitor, and automatic carousel. Pressure and temperature feedbacks were monitored and microwave field power and temperature was adjusted automatically. One half gram (0.50 g) of sample was weighed and quantitatively transferred into a PTFE reaction vessel liner with a pressure relief valve fitted with a PTFE membrane, and placed in a ceramic jacket. The sample was then digested in 8 ml of 70% nitric acid (HNO_3), 4 ml of 48% hydrofluoric acid (HF), and 2 ml of 37% hydrochloric acid (HCl) at 180°C and 20 bar in the microwave until all material was in solution. The digestion liquors were brought to 50 ml total volume by adding 36 ml of 18.2 MΩ deionized water. NIST standard references 1646a (Estuarine Sediment Standard Reference Material) and 2709 (San Joaquin Soil Standard Reference Material) were carried through the same digestion and analytical procedure for recovery verification. The prepared samples were analyzed for total As using a Perkin Elmer AAnalyst 600 graphite furnace-atomic absorption (GFAA) equipped with a Zeeman background correction system at the Sierra Nevada Research Institute Environmental Analytical Lab following The American Society for Testing and Materials (ASTM) Method 3052 (same as EPA Method 3052).

Sediments were analyzed by powder X-ray diffraction (XRD) using a Panalytical X'pert Pro PW3040/50 diffractometer with a Cu anode operating with the following conditions: Generator voltage: 45 kV; tube current: 40 mA; divergence slit: 0.76 mm; receiving slit: 0.76 mm; scan range: 2-70 degrees 2-theta; step size: 0.001 degrees.

Batch and Column Experiments

All chemicals used were reagent grade or higher. Solutions were prepared with 18.2 MΩ deionized water (Millipore Milli-Q system) and stored in plastic containers that had been washed with 3% HNO_3. All volumetric flasks had been washed with 3% HNO_3 and rinsed several times with deionized water prior to use. Deoxygenated water was purged with N_2(g) for at least 15 h per liter, and placed in a N_2-atmosphere glovebox for at least 24 h before use. All solutions were prepared and experiments were conducted in an anaerobic N_2-atmosphere glovebox (Coy Laboratory Products) equipped with an oxygen removal catalyst and oxygen/hydrogen gas analyzer to monitor oxygen. Strict anaerobic conditions were maintained at all times and all As-containing solutions and experiments were shielded from light.

Table SI-1. Synthetic groundwater solution used in batch and column experiments.

NaCl	3.53E-03	M
$CaSO_4$	1.71E-04	M
$CaCl_2$	1.77E-04	M
$MgCl_2$	1.19E-04	M
$Na_2SiO_3 \cdot 9H_2O$	3.20E-04	M
pH (initial)*	6.1	

*pH-buffered experiments included 0.01 M 4-morpholineethanesulfonic acid (MES).

Prior to introduction of As solutions, column flow was characterized with bromide (Br^-) as a conservative tracer. Bromide (Br^-) tracer tests were performed at three different flow rates (0.5, 0.25 and 0.12 ml min^{-1}) at 200 ppm Br^- and measured using 9635BN ThermoOrion electrode. Electrode detection limit was 0.4 ppm Br^- and measurement error was ±2% (Fig. SI-1).

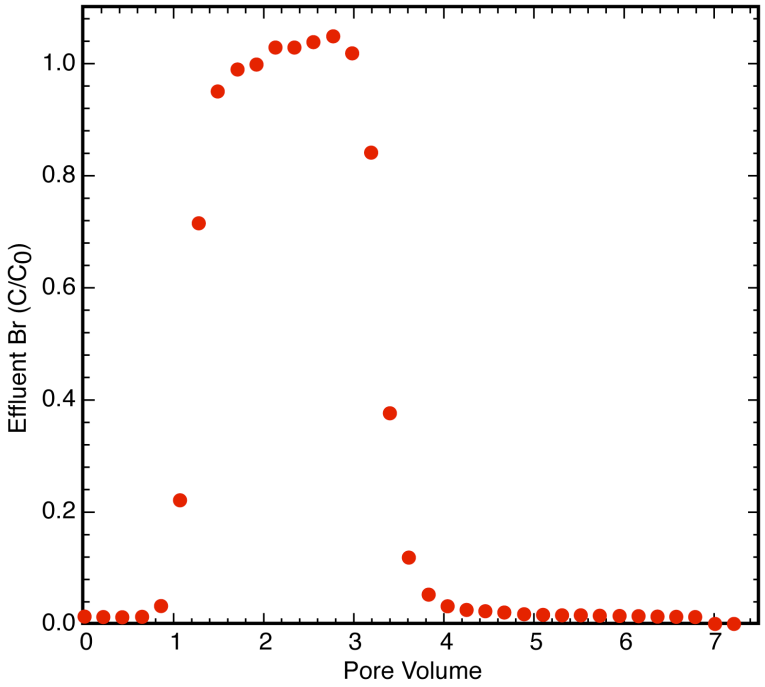

Figure SI-1. Representative effluent concentrations of the conservative Br^- tracer shown as effluent concentration (C) divided by influent concentration (C_0) from one of the sediment columns (Br^- behavior was similar and within error for all column tests).

Analysis of XAS Data

For for the analysis of XAS data, background was subtracted using the pre-edge absorption and normalized to the post-edge absorption (fluorescence/incident energy) using the SIXPACK software package *(3)*. For As and Fe XANES, spectra were fit by least-squares linear combination of reference components. For normalized As XANES, a number of reference As(III) and As(V) compounds and sorption samples were tested in fits. Final binary fits were done using a spectrum of sorbed As(V) (10^{-5} M $[As]_{tot}$) and a spectrum of sorbed As(III) (10^{-3} M $[As]_{tot}$) on SMW-3 composite as end members. Fits of these spectra with several reference compounds verified that each consisted of only As(V) or As(III). These two components most closely matched the spectral background of the column samples because the mineral matrix was

the same in both. Sediment Fe XANES spectra were fit by linear combination of reference Fe minerals from a previously analyzed spectral library *(4)*. Combination fits gave total spectral sums of ±5% of unity without re-normalization of fit totals. Fits of Mn XANES of reacted sediments using reference Mn compounds were not able to produce acceptable results regardless of the number of components used in the fit. This is probably because Mn is present in sediments as a substituent in other mineral phases rather than as a pure Mn phase. Qualitative comparisons were made between the Mn XANES spectra of reacted sediments and reference Mn compounds.

Normalized EXAFS spectra were fit using the program EXAFSPAK *(5)* by non-linear least-squares methods on individual atomic shells in k-space using the entire k-range in the fit (i.e., no reverse Fourier filtering was done; see *(6)*). Theoretical phase-shift and amplitude functions for single and multiple-scattering were calculated with the program FEFF *(7, 8)* using atomic clusters taken from the crystal structures of known arsenic compounds with geometries similar to those expected in the unknown sediment samples. Multiple-scattering (MS) within the As-O tetrahedra was included in the least-squares fit model when the spectrum was all As(V). Our prior analyses of reference compounds and sediment samples showed that MS does not contribute significantly above background scattering to the EXAFS of sediment spectra when only As(III) is present *(9)*.

II. RESULTS

Sediment Characterization

Results for extractable As, Fe, and Mn from core SMW-3 from two depth intervals is given in Table SI-2. The composite sediment used in batch and column experiments was homogenized from these two intervals and from 39.6 m depth, which is similar in color and

lithography to the deeper intervals. The homogenized sample was measured for total As by both EPA Method 3050B and by hydrofluoric acid digestion. Results of the two methods differed by 3% (within analytical error). Percent H_2O was similar among all samples. Some variability in Mn and Fe among the samples at different depths was detected (Table SI-2).

Analysis of bulk sediment XRD indicated that the primary mineral phases were quartz and plagioclase feldspar. Minor diffraction peaks (near detection limit) can be assigned to illite, chlorite, vermiculite or montmorillonite, and kaolinite, although there is overlap of peaks associated with chlorite and kaolinite.

Table SI-2. Total As, Fe, and Mn from sediment SMW-3 by EPA Method 3050B and As concentrations by complete hydrofluoric acid (HF) digestion (mmol kg^{-1} sediment on dry wt. basis).

Depth (m)	As (3050B)	SD[a]	As (HF)	SD[a]	Mn (3050B)	SD[a]	Fe (3050B)	SD[a]	Fe (HF)	SD[a]	% H_2O
41.1[b]	0.216	0.020			4.96	0.300	215.3	14.1			24.6
42.7[b]	0.201	0.003			6.04	0.032	249.0	3.21			23.4
Hom.[c]	0.194	0.006	0.203	0.002	n.m.[d]		257.1	4.24	262.6	2.08	21.5

[a] S.D.: standard deviation of triplicate samples.
[b] Sample from He et al. *(2)*
[c] Homogenized SMW-3 is a mixture of homogenized sediment samples from depths of 39.6, 41.1 and 42.7 m collected at SMW-3; 3050B extraction used HCl rather than H_2O_2 (see *(1)*).
[d] n.m.: not measured.

Sorption Data

Table SI-3 lists the results of batch experiments with composite sediment SMW-3 shown in manuscript, Figure 1.

Table SI-3. Batch experiments of dissolved As sorption and Mn and Fe release with Devens composite sediment SMW-3[a].

As(III) initial (μM)	As(tot) final (μM)	SD	% As sorbed	SD	As sorbed (mmol kg^{-1} sediment)	SD	As(tot, u) final[c] (μM)	SD[c]	% As sorbed[c]	SD[c]	As sorbed[c] (mmol kg^{-1} sediment)	SD[c]	Mn(aq) (μM)	SD	Fe(aq) (μM)	SD
control	0.042	0.004											0.657	0.123	0.317	0.068
992	754	3.44	24.0	0.347	6.51	0.044	725	4.88	27.0	0.492	7.30	0.078	3.57	0.027	7.91	4.74
98.8	66.0	1.28	33.2	1.29	0.789	0.073	72.9	8.53	26.2	8.63	0.639	0.288	1.17	0.171	1.46	0.481
10.0	4.64	0.198	53.6	1.98	0.146	0.006	5.27	0.162	47.4	1.62	0.129	0.004	0.744	0.030	1.06	0.422
0.957	0.263	0.055	72.5	5.71	0.019	0.002	0.254	0.011	73.4	1.16	0.019	0.000	0.642	0.043	0.803	0.295
As(V) initial (μM)																
control	0.049	0.003											0.461	0.128	0.494	0.063
1034	728	6.79	29.6	0.66	8.08	0.044	699	45.1	32.4	4.36	8.87	1.043	0.669	0.058	1.90	0.158
95.2	57.2	2.70	39.9	2.84	1.013	0.047	68.4	11.2	28.2	11.8	0.712	0.281	0.563	0.016	2.88	1.33
11.1	1.17	0.058	89.4	0.521	0.265	0.000	1.32	0.142	88.1	1.28	0.261	0.002	0.469	0.065	2.90	0.756
1.06	0.061	0.003	94.2	0.323	0.026	0.000	0.049	0.001	95.4	0.135	0.026	0.000	0.583	0.036	1.11	0.592
As(III) initial (ST)[b] (μM)																
control	0.053	0.002											0.708	0.050	0.641	0.272
1025	771	7.98	24.8	0.779	6.61	0.019	741	5.37	27.6	0.524	7.39	0.394	4.65	0.238	10.8	2.58
99.9	71.8	3.26	28.1	3.26	0.749	0.097	69.1	2.65	30.8	2.65	0.818	0.060	1.92	0.291	1.78	0.217
10.7	5.75	0.076	46.4	0.713	0.134	0.003	6.40	0.058	40.2	0.537	0.116	0.006	1.68	0.014	0.885	0.125
1.04	0.400	0.010	61.7	0.982	0.017	0.000	0.528	0.001	49.4	0.140	0.013	0.000	1.62	0.034	1.13	0.173
As(V) initial (ST)[b] (μM)																
control	0.062	0.018											0.679	0.150	0.738	0.014
1116	800	7.37	28.4	0.661	8.61	0.463	807	14.9	27.7	1.33	8.40	0.661	1.24	0.175	0.605	0.189
92.7	58.6	0.787	36.8	0.849	0.893	0.021	62.1	2.50	33.0	2.70	0.800	0.065	0.962	0.120	0.321	0.133
10.2	1.40	0.206	86.2	2.02	0.233	0.007	1.85	0.299	81.8	2.94	0.221	0.004	1.56	0.051	0.669	0.293
0.989	0.088	0.009	91.1	0.875	0.024	0.000	0.063	0.002	93.7	0.157	0.025	0.000	1.65	0.036	0.716	0.331

[a] 24 h equilibration in the dark of replicate samples; SD is standard deviation of replicate analyses. Sorption calculated using measured sediment dry weight (~0.8 g sediment). [b] ST is sterilized with 2% formaldehyde. [c] unfiltered samples; all other samples filtered (0.45 μm nylon filters) before analysis.

Table SI-4. Summary of CFITM results and integrated uptake and desorbed amounts of As, Fe, and Mn from column experiments.

Physical Parameters		Column[a]		
		1	2	3
Sediment mass (kg, dry)		0.0893	0.0880	0.0885
Pore volume (cm^3)		17.8	18.3	18.1
Br^- [b]	Peclet number	41.0	40.4	43.8
As[c]	Retardation (R)	15.5	48.2	62.5
	partition coeff. (β)	0.53	0.33	0.29
	mass transfer coeff. (ω)	0.56	0.50	0.47
Uptake and Desorption[d]				
As	sorbed (mmoles)	0.0462	0.0801	0.0685
	sorbed (mmol/kg sed.)	0.518	0.910	0.774
	desorbed (mmoles)	0.0293	0.0605	0.0556
	net sorbed (mmol/kg sed.)	0.189	0.222	0.146
	% net sorbed	36.6	24.4	18.9
Fe	sorbed (mmoles)	n.a.	1.14	1.57
	sorbed (mmol/kg sed.)	n.a.	13.0	17.7
	desorbed (mmoles)	n.a.	0.459	0.493
	net sorbed (mmol/kg sed.)	n.a.	7.76	12.1
	% net sorbed	n.a.	59.8	68.5
	Fe sorbed/As sorbed (net)	n.a.	35.0	82.9
Mn	desorbed (mmoles)	0.0338	0.148	0.133
	desorbed (mmol/kg sed.)	0.378	1.69	1.51
	Mn desorbed/As sorbed	2.0	7.6	10.3

[a] Empty column volume = 51.5 cm^3; sediment bulk density = 2.65 g cm^{-3}. Influent solutions (sterilized with formaldehyde): Column 1: 10^{-4} M As(III); Columns 2 (unbuffered) and 3 (buffered): 10^{-4} M As(III) + 10^{-3} M Fe(II).

[b] Conservative Br^- fit using an equilibrium model with retardation factor (*R*) fixed at 1.0.

[c] Fit using a non-equilibrium model with Peclet number from Br^- fit.

[d] Calculated from integration of element uptake and release (Manuscript, Fig. 2); n.a. = not applicable.

Transport parameters were determined by curve fitting of the analytical solution of the advection-dispersion equation to the measured breakthrough curves with the CFITM code of van Genuchten *(10)*. Breakthrough of the conservative tracer (Br^-; see Fig. SI-1) was fit using the equilibrium model in CFITM with retardation factor (*R*) fixed at 1.0 to determine a Peclet number (Pe= vL/D, where v is average pore water velocity, L is length, and D is the dispersion coefficient). A non-equilibrium model was used to fit As breakthrough, where the partition

coefficient (β) and the mass transfer coefficient (ω) were determined by nonlinear least-squares curve fitting, using a fixed Peclet number from the Br^- tracer fits.

XAS Results

The extended X-ray absorption fine structure (EXAFS) spectrum was collected for two batch samples (10^{-3} M As(III) or As(V)) to verify the sorption mechanism. The EXAFS spectra showed a prominent first shell corresponding to oxygen ligands and weak backscattering from near-neighbor atoms beyond the first shell (Fig. SI-1). The spectra were fit quantitatively assuming second-neighbor Fe shells as representive of metal backscattering atoms in sediment minerals. Fits including second-neighbor backscattering atoms were statistically better than fits assuming only first shell O atoms. Interatomic distances determined from best fits correspond to expected distances for bidentate sorption of As(III) and As(V) determined in previous studies of reference compounds *(9, 11, 12)* (Table SI-4). Fit results indicated low coordination numbers of second-neighbor atoms, consistent with adsorption of As on sediment minerals (rather than incorporation into mineral structures) as the primary mechanism of retention.

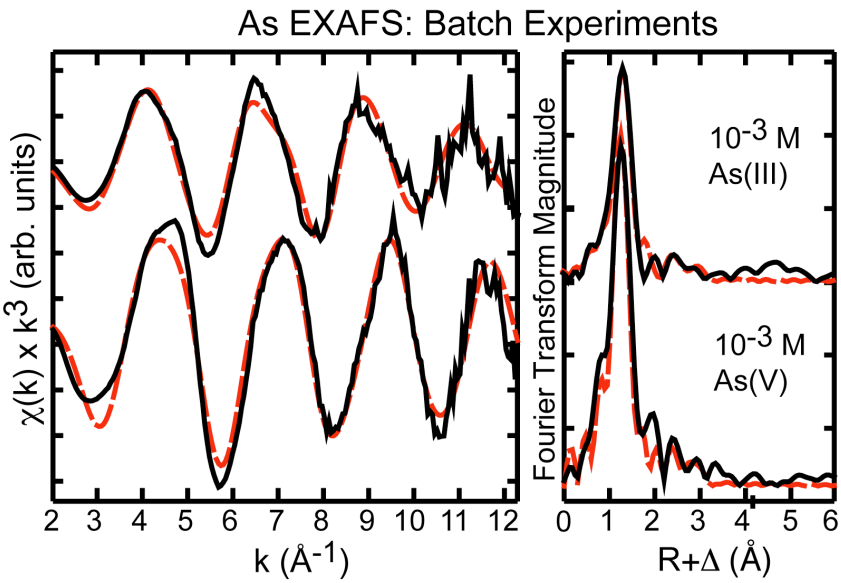

Figure SI-2. Arsenic EXAFS spectra and Fourier transforms of batch sediments reacted with 10^{-3} M As(III) or As(V). Dashed line is the non-linear least-squares best fit (numerical results below).

Table SI-5. Results of As EXAFS fits.

Batch Sample	A-B	N	R (Å)	σ^2 $(Å)^2$	ΔE_0 (eV)	Reduced χ^2
As(III) 10^{-3} M	As-O	3.4*	1.77*	0.0040	-0.06*	0.90
	As-Fe	0.5*	2.93*	0.0080		
	As-Fe	0.4*	3.37*	0.0080		
As(V) 10^{-3} M	As-O	4	1.69*	0.0024*	-0.26*	1.45
	As-MS1	1	3.03/	0.0036/		
	As-Fe	0.8*	3.32*	0.0080		

* parameter varied in least-squares fit.
/ parameter link to preceeding table entry in least-squares fit.
A-B is the absorber-backscatterer pair; N is the number of backscatterers; R is the distance between A-B; σ^2 is a Deby-Waller disorder parameter; ΔE_0 is the threshold energy difference; χ^2 is a reduced least-squares goodness-of-fit parameter. MS1 is from multiple scattering between As and O in the arsenate tetrahedron. Fixed Debye-Waller factors taken from *(9)*.

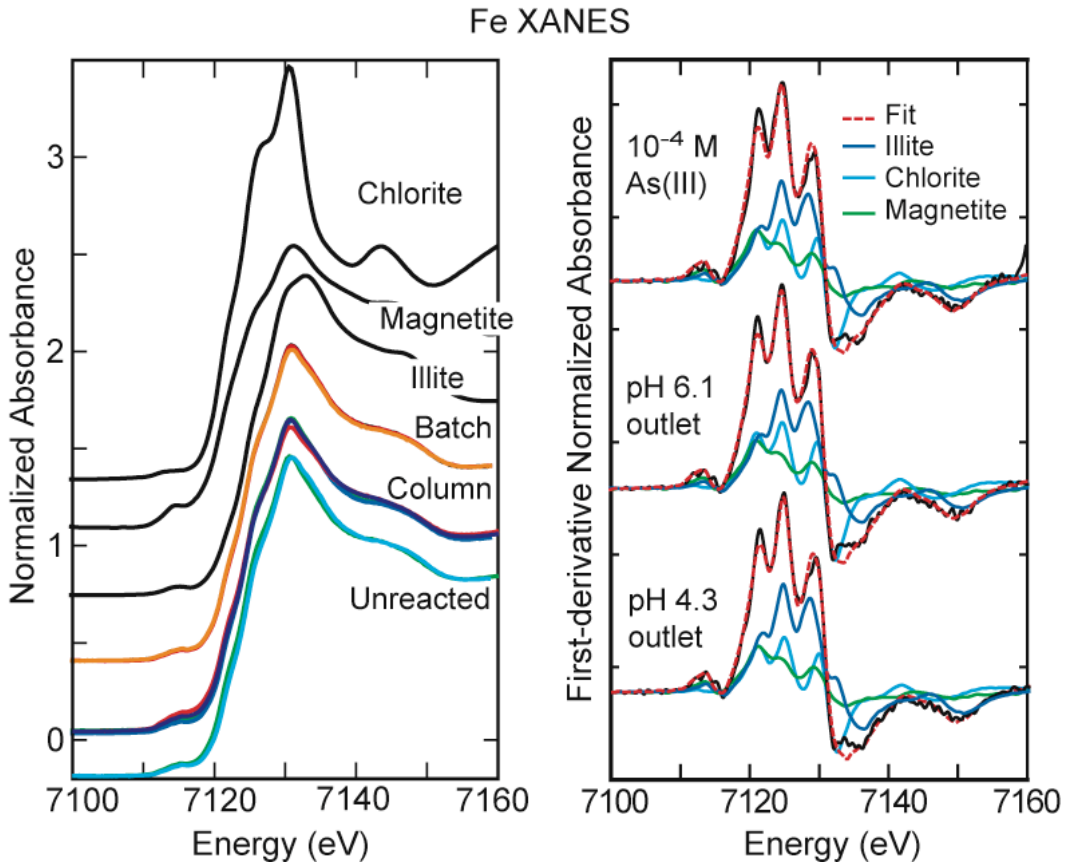

Figure SI-3. A. Normalized Fe XANES spectra (left panel) of batch sediments reacted with As(III) solutions (10^{-3}, 10^{-4}, 10^{-5} M), reacted column sediments (Columns 2 and 3, As(III) 10^{-4} M + Fe(II) 10^{-3} M, inlet and outlet), and two unreacted SMW-3 sediments (composite and 42.7 m depth). Reference compounds are: natural Fe-chlorite (ripidolite, CCa-2) and natural illite (IMt-1), both from Clay Mineral Society Source Clays Repository, and natural magnetite (a-FeO_3O_4). First-derivative spectra (right panel) shows fit deconvolutions of reference mineral spectra for batch and column spectra. Numerical fit results reported in Table SI-6.

Table SI-6. Iron XANES fit results for batch and column experiments.

Sample	Component	Fraction	Total	Energy Shift[a] (ΔeV)
Batch Experiments				
As(III) 10^{-3} M	Chlorite	0.20	0.98	0.08
	Illite	0.54		
	Magnetite	0.24		
As(III) 10^{-4} M	Chlorite	0.21	0.99	0.14
	Illite	0.47		
	Magnetite	0.31		
As(III) 10^{-5} M	Chlorite	0.21	0.98	0.09
	Illite	0.48		
	Magnetite	0.29		
unreacted SMW-3 (composite)	Chlorite	0.19	0.98	0.08
	Illite	0.55		
	Magnetite	0.24		
unreacted SMW-3 (140 ft)	Chlorite	0.18	0.98	0.08
	Illite	0.52		
	Magnetite	0.28		
Columns 2 (pH 4.3) and 3 (pH 6.1): 10^{-4} M As(III) + 10^{-3} M Fe(II) (ST)[b]				
pH = 4.3 Outlet	Chlorite	0.18	0.97	0.26
	Illite	0.51		
	Magnetite	0.28		
pH = 4.3 Inlet	Chlorite	0.15	0.92	0.25
	Illite	0.39		
	Magnetite	0.38		
pH = 6.1 Outlet	Chlorite	0.22	0.97	0.27
	Illite	0.47		
	Magnetite	0.28		
pH = 6.1 Inlet	Chlorite	0.19	0.95	0.26
	Illite	0.48		
	Magnetite	0.28		

[a] Treated as a single variable parameter for all fit components.
[b] ST is sterilized with addition of 2% formaldehyde.

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